

The H_2^+ molecular ion: low-lying states

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Abstract

Combining the WKB expansion at large distances and Perturbation Theory at small distances it is constructed a compact uniform approximation for eight low-lying eigenfunctions: with the quantum numbers (n, m, Λ, \pm) , where $n = m = 0$ at $\Lambda = 0, 1, 2$, and $n = 1, m = 0$ at $\Lambda = 0$. For any of these states this approximation provides the relative accuracy $\lesssim 10^{-5}$ (not less than 5 s.d.) for any real x in eigenfunctions and for total energy $E(R)$ it gives 10-11 s.d. for internuclear distances $R \in [0, 50]$. Corrections to proposed approximation are evaluated systematically in a framework of the convergent perturbation theory. Separation constants are found with 8 s.d. The oscillator strength for the electric dipole transitions are accurately calculated and compared with existing data with coincidence on the level of 7 s.d. The magnetic dipole and electric quadrupole transitions are accurately calculated for the first time with not less than 7 s.d.

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INTRODUCTION

The simplest molecular system which appears in Nature is the H_2^+ molecular ion. Needless to say that this system plays a fundamental role in different physical sciences, in particular, in atomic-molecular physics, in laser and plasma physics being also a traditional example of two-center Coulomb system (Z, Z, e) which enters to all QM textbooks (see e.g. [1]). Due to the fact that protons are much more heavy than electron a standard consideration of the problem is made in the so-called static approximation (or, in other words, in the Bohr-Oppenheimer approximation of the zero order). In this approximation the protons are simply assumed to be infinitely heavy. It can be immediately checked that the projection of the angular momentum to the molecular axis (the line connecting the proton positions) L_ϕ is preserved, $[L_\phi, \mathcal{H}] = 0$, where \mathcal{H} is the Hamiltonian. Thus, the angular variable ϕ can be separated out. Hence, the problem is reduced to two-dimensional, which admits itself the separation of variables in elliptic coordinates. It reflects a unique property of general two-center Coulomb problem (Z_1, Z_2, e) of the complete separation of variables (in prolate ellipsoidal coordinates).

In general, two-center Coulomb problem (Z, Z, e) is non-solvable exactly, it can be solved in approximate way only. Thus, we need to introduce a natural definition of *solvability* of non-solvable spectral problem: for any eigenfunction Ψ we can indicate constructively an uniform approximation Ψ_{app} such that

$$\left| \frac{\Psi(x) - \Psi_{app}(x)}{\Psi_{app}(x)} \right| \lesssim 10^{-\delta}, \quad (1)$$

in the coordinate space. In vicinity of the nodal surface, $\Psi_{app}(x) = 0$ the absolute deviation

$$|\Psi(x) - \Psi_{app}(x)| \lesssim 10^{-\delta}, \quad (2)$$

where the parameter $\delta > 0$ characterizes a number of significant digits (s.d.), which the approximation reproduces exactly. It implies that any observable, any matrix element can be found with accuracy not less than δ .

A simple idea we are going to employ in order to construct an approximation is to combine WKB-expansion at large distances with perturbation theory at small distances near extremum the potential for the phase of wavefunction in a single interpolation. In the case of excited states this interpolation was complemented by a polynomial factor which carried

the information about nodes. This idea was realized successfully for quartic anharmonic oscillator [2] and double-well potential [3]. In both cases for the lowest states it was constructed two-three parametric uniform approximations of the phase of eigenfunction leading to 10 s.d. in energies and with $\delta \sim 5 - 6$ for any value of the coupling constant and size of the barrier. Recently, we announced the results of the similar quality for two lowest (and the most important) states $1s\sigma_g$ and $2p\sigma_u$ of the H_2^+ molecular ion [4]. A few parametric approximation leading to $\delta \sim 5 - 6$ was found. The goal of this paper is to extend and profound this analysis constructing approximations with $\delta \sim 5 - 6$ for eight low lying states of the H_2^+ molecular ion, including two above mentioned states. In order to check accuracy of obtained approximations a special convergent perturbation theory (PT) is developed. This PT allows us to evaluate a local deviation of the approximation from the exact eigenfunction. Eventually, we calculate systematically separation constants and the oscillator strength for the electric dipole and quadrupole, and magnetic dipole transitions.

It is worth mentioning that a study of the wavefunctions of the H_2^+ molecular ion in a form of expansion in some basis was initiated by Hylleraas [5] and was successfully realized in the remarkable paper [6] (see also [7, 8]). Attempts to find bases leading to fast convergence are still continuing. At present, the basis of pure exponential functions seems the most fast convergent (see e.g. [9] and references therein). Let us notice that following the analysis of classical mechanics of the H_2^+ system and its subsequent semiclassical quantization it was attempted to build some uniform approximations of wavefunctions of low lying electronic states [10]. Local accuracies of these approximations are unclear whilst eigenvalues are found with a few significant digits.

I. GENERALITIES

The Schrödinger equation, which describes the electron in the field of two fixed centers of the charges Z_1, Z_2 at the distance R , is of the form

$$\left(-\Delta - \frac{2Z_1}{r_1} - \frac{2Z_2}{r_2}\right)\Psi = E'\Psi, \quad \Psi \in L^2(\mathbf{R}^3), \quad (3)$$

where $E' = (E - \frac{2Z_1Z_2}{R})$ and the total energy E are in Rydbergs, $r_{1,2}$ are the distances from electron to first (second) center, respectively. Following [1] let us introduce the dimensionless

2D elliptic coordinates and azimuthal angle φ with respect to the molecular axis [22]:

$$\xi = \frac{r_1 + r_2}{R}, \quad \eta = \frac{r_2 - r_1}{R}, \quad 1 \leq \xi \leq \infty, \quad -1 \leq \eta \leq 1. \quad (4)$$

In these coordinates the Coulomb singularities are situated at

$$\xi = 1, \quad \eta = \pm 1,$$

being at the boundaries of the configuration space. The Jacobian is $\propto (\xi^2 - \eta^2)$. The equation (3) admits separation of variables in (4). Since the projection of the angular momentum to the molecular axis \hat{L}_ϕ commutes with the Hamiltonian [23] the eigenstate has a definite magnetic quantum number Λ . If $Z_1 = Z_2$ the Hamiltonian is permutationally-symmetric $r_1 \leftrightarrow r_2$, or, equivalently, $\eta \rightarrow -\eta$, hence, any eigenfunction is of a definite parity (\pm). As a result, it can be represented in a form

$$\Psi = X(\xi)(\xi^2 - 1)^{\Lambda/2} Y(\eta)(1 - \eta^2)^{\Lambda/2} e^{\pm i\Lambda\phi}, \quad \Lambda = 0, 1, 2, \dots \quad (5)$$

where $Y(\eta)$ is of definite parity. Following the analysis we introduce the notation for a state as (n, m, Λ, \pm) where $n, m = 0, 1, \dots$ are the quantum numbers in ξ and η coordinates, respectively, they have a meaning of number of nodes in ξ and η , Λ is a magnetic quantum number and \pm is parity. It is easy to check that the ground state with the lowest total energy is $(0, 0, 0, +)$.

The factors $(\xi^2 - 1)^{\Lambda/2}$ and $(1 - \eta^2)^{\Lambda/2}$ are introduced (5) to take into account a singular behavior of the eigenfunction near Coulomb singularities. After substitution of the representation (5) into (3) we arrive at the equations for $X(\xi)$ and $Y(\eta)$,

$$\partial_\xi[(\xi^2 - 1)\partial_\xi X] + 2\Lambda\xi\partial_\xi X + [-p^2\xi^2 + 2R\xi + A]X = 0, \quad X \in L^2(\xi \in [1, \infty)), \quad (6)$$

$$\partial_\eta[(\eta^2 - 1)\partial_\eta Y] + 2\Lambda\eta\partial_\eta Y + [-p^2\eta^2 + A]Y = 0, \quad Y \in L^2(\eta \in [-1, 1]), \quad (7)$$

respectively, where following [6] we denote,

$$p^2 = -\frac{E'R^2}{4}, \quad (8)$$

and A is a separation constant. Equations (6), (7) define a bispectral problem with E, A as spectral parameters for any given R . Square-integrability of the function Ψ (5) implies a non-singular behavior of X at $\xi \rightarrow 1$ and decay at $\xi \rightarrow \infty$ as well as non-singular behavior

of Y at $\eta \rightarrow \pm 1$. Such a non-singular solution X can be continued from the interval $[1, +\infty)$ to the whole line $(-\infty, +\infty)$. It implies searching a solution of the spectral problem (6) which grows at $\xi \rightarrow -\infty$, decays at $\xi \rightarrow +\infty$ being a constant at $\xi = 1$. A non-singular solution $Y(\eta)$ at $\eta = \pm 1$ can be unambiguously continued in η beyond the interval $[-1, 1]$ to $(-\infty, +\infty)$, it corresponds to growing (non-decaying) at $|\eta| \rightarrow \infty$.

The equation (6) formally coincides with equation (7) at $R = 0$ (united atom limit). It is evident that a domain for (7) is extended to $[1, \infty)$ it has no L^2 solutions since there is no degeneracy at any R with $R = 0$. Hence, at E, A the solution found at the equation (6) should be non-normalizable solution. Since at $R = 0$ the problem becomes one-center Coulomb problem and can be solved exactly, the above consideration can be checked explicitly. It is also in agreement with large- η behavior of the Hund-Mulliken function (it mimics the incoherent interaction of electron with charged centers) for both $1s\sigma_g$ (parity +) and $2p\sigma_u$ (parity -) states

$$\Psi_{HM}^{(\pm)} = e^{-2\alpha_2 r_1} \pm e^{-2\alpha_2 r_2} = 2e^{-\alpha_2 R\xi} \begin{bmatrix} \cosh(\alpha_2 R\eta) \\ \sinh(\alpha_2 R\eta) \end{bmatrix}, \quad (9)$$

which describes large R behavior. Similarly, for the Guillemin-Zener function (it mimics the coherent interaction of electron with charged centers) we get

$$\Psi_{GZ}^{(\pm)} = e^{-2\alpha_3 r_1 - 2\alpha_4 r_2} \pm e^{-2\alpha_3 r_2 - 2\alpha_4 r_1} = 2e^{-(\alpha_3 + \alpha_4)R\xi} \begin{bmatrix} \cosh((\alpha_3 - \alpha_4)R\eta) \\ \sinh((\alpha_3 - \alpha_4)R\eta) \end{bmatrix}, \quad (10)$$

which has to describe small R behavior.

A. Asymptotics.

If we assume a representation $X = e^{-\varphi}$, then the WKB-expansion of phase at $\xi \rightarrow \infty$,

$$\varphi = p\xi - \left(\frac{R}{p} - \Lambda - 1\right) \log \xi + \left[\frac{A + (\frac{R}{p} - \Lambda - 1)(\frac{R}{p} + \Lambda)}{p} - p \right] \frac{1}{2\xi} + \dots, \quad (11)$$

while at $\xi \rightarrow 0$,

$$\varphi = -\frac{A}{2}\xi^2 - \frac{R}{3}\xi^3 + \frac{(p^2 + A^2 - A(2\Lambda + 3))}{12}\xi^4 + \dots. \quad (12)$$

Similarly to X if we put $Y = e^{-\varrho}$, then at $\eta \rightarrow \infty$,

$$\varrho = -p\eta + (\Lambda + 1) \log \eta - \left(\frac{A - \Lambda(\Lambda + 1)}{p} - p \right) \frac{1}{2\eta} + \dots, \quad (13)$$

when at $\eta \rightarrow 0$,

$$\varrho = -\frac{A}{2}\eta^2 + \frac{(p^2 + A^2 - A(2\Lambda + 3))}{12}\eta^4 + \dots \quad (14)$$

The important property of the expansions (11) and (13) is that the coefficients in front of the growing terms at large distances (linear and logarithmic) are found explicitly, since they do not depend on the separation constant A .

B. Approximation

Making interpolation between WKB-expansion (11) and the perturbation theory (12) for X , (13) and (14) for Y , correspondingly, and taking into account that the Z_2 -symmetry of Ψ : $\eta \rightarrow -\eta$ is realized through use of cosh(sinh)-function (cf. (9) and (10)) we arrive at the following expression [4]

$$\Psi_{n,m,\Lambda}^{(\pm)} = \frac{(\xi^2 - 1)^{\Lambda/2} P_n(\xi)}{(\gamma + \xi)^{1+n+\Lambda-\frac{R}{p}}} e^{-\xi \frac{\alpha+p\xi}{\gamma+\xi}} \frac{(1 - \eta^2)^{\Lambda/2} Q_m(\eta^2)}{(1 + b_2\eta^2 + b_3\eta^4)^{\frac{1+2m+\Lambda}{4}}} \left[\frac{\cosh \left(\eta \frac{a_1 + pa_2\eta^2 + pb_3\eta^4}{1 + b_2\eta^2 + b_3\eta^4} \right)}{\sinh \left(\eta \frac{a_1 + pa_2\eta^2 + pb_3\eta^4}{1 + b_2\eta^2 + b_3\eta^4} \right)} \right] e^{\pm i\Lambda\phi}, \quad (15)$$

for the eigenfunction of the state with the quantum numbers (n, m, Λ, \pm) . Here α, γ and $a_{1,2}, b_{2,3}$ are parameters (see below), $P_n(\xi)$ and $Q_m(\eta^2)$ are some polynomials of degrees n and m with real coefficients with n and m real roots in the intervals $[1, \infty)$ and $[0, 1]$, respectively. One can choose these polynomials to ensure their orthogonality to all states with lower total energies.

II. RESULTS

A. Ground state of positive/negative parity

Let us consider two lowest states - one of positive and one of negative parity, $1s\sigma_g$ $(0, 0, 0, +)$ and $2p\sigma_u$ $(0, 0, 0, -)$, respectively, following the consideration [4]. Corresponding approximations have the form

$$\begin{aligned} \Psi_{0,0,0}^{(\pm)} &= \frac{1}{(\gamma + \xi)^{1-\frac{R}{p}}} e^{-\xi \frac{\alpha+p\xi}{\gamma+\xi}} \frac{1}{(1 + b_2\eta^2 + b_3\eta^4)^{1/4}} \left[\frac{\cosh \left(\eta \frac{a_1 + pa_2\eta^2 + pb_3\eta^4}{1 + b_2\eta^2 + b_3\eta^4} \right)}{\sinh \left(\eta \frac{a_1 + pa_2\eta^2 + pb_3\eta^4}{1 + b_2\eta^2 + b_3\eta^4} \right)} \right] \\ &\equiv X_0(\xi) Y_0^{(\pm)}(\eta), \end{aligned} \quad (16)$$

(cf. (15)), respectively, and each of them depends on six parameters α, γ and $a_{1,2}, b_{2,3}$. The easiest way to find these parameters is to make a variational calculation taking (16) as a trial function for R fixed and with p as an extra variational parameter. Immediate striking result of the variational study is that for all $R \in [1, 50]$ the optimal value of the parameter p coincides with the exact value of p (see (8)) with extremely high accuracy for both $1s\sigma_g$ and $2p\sigma_u$ states. It implies a very high quality of the trial function - the variational optimization wants to reproduce with very high accuracy a domain where the eigenfunction is exponentially small, hence, the domain which gives a very small contribution to the energy functional. In Tables I and II the results for the total energy (as well as for sensitive p) vs R of $1s\sigma_g$ and $2p\sigma_u$ states are shown as well as their comparison with ones obtained by Montgomery [7] in highly-accurate realization of the approach by Bates et al [6], and also with the results we obtained in the Lagrange mesh method based on Vincke-Baye approach [13] (details will be given elsewhere). For all studied values of R for both $1s\sigma_g$ and $2p\sigma_u$ states our variational energy turns out to be in agreement on the level of 10 s.d. with these two alternative calculations. Variational parameters are smooth slow-changing functions of R , see Tables III-IV. All calculations were implemented in double precision arithmetics and checked in quadruple precision one. It is worth noting that the number of optimization parameters can be reduced putting $a_2 = b_2 = 0$, however, in this case the accuracy in energy drops from 10-11 to 5-6 significant digits.

Hence, our relatively-simple, few parametric functions (16) taken as trial functions in a variational study provide very high accuracy in energy in comparison with highly-accurate alternative calculations. Two naturally related questions occur: (i) can we estimate the accuracy of variationally obtained energies without making a comparison with other calculations and (ii) how close locally our functions to the exact ones in configuration space. In order to answer these questions we develop a perturbation theory for the Schroedinger equation (3) taking a trial function (16) as zero approximation.

Let us choose X_0, Y_0 (16) with parameters fixed variationally (see above) as zero approximation in perturbation theory (30), (36) (see Appendix). It is evident that by construction of X_0, Y_0 the emerging perturbation theory has to be convergent. Assuming the condition (42) is fulfilled for the first corrections, namely, $A_{1,\xi} = A_{1,\eta} = A_1$, we find the first corrections

$\varphi_1(\xi)$ and $\varrho_1(\eta)$ as functions of A_1 . Then we modify the trial function (16),

$$\Psi_{0,0,0}^{(\pm)} \rightarrow X_0(\xi)Y_0^{(\pm)}(\eta) e^{-\varphi_1(\xi)-\varrho_1(\eta)} \quad (17)$$

and make the variational calculation with this trial function minimizing with respect to parameter p . The (expected) result is that the optimal value of parameter p remained unchanged with respect to the value obtained for the trial function (16) with extremely high accuracy - within 10 s.d.! It indicates that the condition (42) is fulfilled with high accuracy. The variational energy is changed beyond the 10 s.d. Therefore, the our energies presented in Tables I, II are correct in all digits. The separation parameters $A_{1,\xi}, A_{1,\eta}$ are presented in Table VII together with those corresponding to other states (see below) . It allows us to find explicitly $\varphi_1(\xi)$ and $\varrho_1(\eta)$. As an illustration in Figs. 1, 2, 3 and 4 the functions $X_0(\xi)$, $Y_0^{(\pm)}(\eta)$ and the first correction to the phases are shown for $R = 2$ a.u. Similar behavior appears for other values of R .

B. $(0, 0, \Lambda, \pm)$ states with $\Lambda = 1, 2$

As the further check the quality of the approximation (15) proposed in [4], we considered the states with magnetic quantum number $\Lambda = 1, 2$ and both parities (\pm) . These four states $(0, 0, 1, +)$, $(0, 0, 1, -)$, $(0, 0, 2, +)$ and $(0, 0, 2, -)$ correspond to the states $2p\pi_u$, $3d\pi_g$, $3d\delta_g$ and $4f\delta_u$ in the united atom nomenclature, respectively. The approximation takes the form

$$\Psi_{0,0,\Lambda}^{(\pm)} = \frac{(\xi^2 - 1)^{\Lambda/2} e^{-\xi \frac{\alpha+p\xi}{\gamma+\xi}}}{(\gamma + \xi)^{1+\Lambda-\frac{R}{p}}} \frac{(1 - \eta^2)^{\Lambda/2}}{(1 + b_2\eta^2 + b_3\eta^4)^{\frac{1+\Lambda}{4}}} \left[\frac{\cosh}{\sinh} \left(\eta \frac{a_1 + pa_2\eta^2 + pb_3\eta^4}{1 + b_2\eta^2 + b_3\eta^4} \right) \right] e^{\pm i\Lambda\phi}, \quad (18)$$

for positive and negative parity, respectively; it depends on six free parameters α, γ and $a_{1,2}, b_{2,3}$ as well as p which can be taken as an extra variational parameter. Due to the presence of the last factor in $\Psi_{0,0,\Lambda}^{(\pm)}$ the function (18) is orthogonal to (16). Taking (18) as a trial function and using the variational method, the optimized values of these parameters are obtained for each fixed value of the internuclear distance R . The results for the total energy and the value of p for the states with $\Lambda = 1, 2$ and both parities (\pm) as a function of the internuclear distance R are presented in Table V. For each R -value, the second line are the results presented by Madsen and Peek [18]. In general, the agreement is on the level of 10 s.d. except for a few values of R where the agreement is on 8 – 9 s.d. On Figs. 5, 6, 7, 8, 9,

TABLE I: The total energy $E_t(R)$ for $1s\sigma_g$ state of the H_2^+ -ion compared to [7] (rounded) and Lagrange mesh method.

R[a.u.]	E_t [Ry] (Present/[7]/Mesh)	p
	-0.90357262676	0.8519936
1.0	-0.90357262676	
	-0.90357262676	
	-1.20526923821	1.483403
1.997193	—	
	-1.20526923821	
	-1.20526842899	1.485015
2.0	-1.20526842899	
	-1.20526842899	
	-1.0239380968	3.49506
6.0	-1.0239380969	
	-1.0239380969	
	-1.0011574578	5.47987
10.0	-1.0011574579	
	-1.0011574579	
	-1.0002611115	6.73221
12.5	—	
	-1.0002611116	
	-1.0000055815	15.492
30.0	—	
	-1.0000055815	
	-1.0000017622	20.4939
40.0	—	
	-1.0000017622	
	-1.0000007211	25.49511
50.0	—	
	-1.0000007211	

TABLE II: The total energy $E_t(R)$ for $2p\sigma_u$ state of the H_2^+ -ion compared to [7] (rounded) and Lagrange mesh method.

R [a.u.]	E_t (Present/[7]/Mesh) [Ry]	p
	0.8703727499	0.5314196
1.0	0.8703727498	
	0.8703727498	
	-0.3332800331	1.1536645
1.997193	—	
	-0.33328003316	
	-0.3350687844	1.155452
2.0	-0.3350687844	
	-0.3350687844	
	-0.8911012787	2.3589
4.0	-0.8911012787	
	-0.8911012787	
	-0.9998021372	5.47678
10.0	-0.9998021372	
	-0.9998021372	
	-1.0001215811	6.75434
12.54525	—	
	-1.0001215811	
	-1.0000283953	10.4882
20.0	-1.0000283953	
	-1.0000283953	
	-1.0000055815	15.492
30.0	—	
	-1.0000055815	
	-1.0000017622	20.4939
40.0	—	
	-1.0000017622	

TABLE III: The parameters of the function (16) for $1s\sigma_g$ state of the H_2^+ -ion. The parameters α, γ and $a_{1,2}, b_{2,3}$ are found via minimization.

	$R_{eq}=1.997193$ a.u.	$R=6.0$ a.u.	$R=20.0$ a.u.
α	1.48407	3.32381	10.0453
p	1.483403	3.49506	10.4882
γ	1.0299	0.96357	0.95774
a_1	0.9164	2.597355	9.8775
a_2	0.05384	0.53443	6.8392
b_2	0.06	0.588072	6.9016
b_3	0.00011	0.00552	1.352

TABLE IV: The parameters of the function (16) for $2p\sigma_u$ state of the H_2^+ -ion. The parameters α, γ and $a_{1,2}, b_{2,3}$ are found via minimization.

	$R=6.0$ a.u.	$R_{min}=12.54525$ a.u.	$R=20.0$ a.u.
α	3.24715	6.5275	10.7397
p	3.43971	6.75434	10.4882
γ	0.95706	0.97045	1.03027
a_1	2.84566	6.075	9.8077
a_2	0.22098	1.46757	2.3784
b_2	0.23611	1.5349	2.43705
b_3	-0.0027	0.1675	0.367

10,11 and 12 the trial functions $X_0(\xi), Y_0^{(\pm)}(\eta)$ and the first corrections to the phases $\varphi_1(\xi)$ and $\varrho_1(\eta)$ for $R = 2$ a.u. are present. We must emphasize that the variational parameter p in Table V coincides with the value of p found from the variational energy, (8) on the level of 5 -9 s.d. It indicates a very high quality of the function (18).

TABLE V: Total energy $E_t(R)$ for the $(0, 0, \Lambda = 1, 2, \pm)$ states of the H_2^+ -ion compared to [18] (second line).

R(a.u.)	$E_t(0, 0, 1, +)$	$p(0, 0, 1, +)$	$E_t(0, 0, 1, -)$	$p(0, 0, 1, -)$	$E_t(0, 0, 2, +)$	$p(0, 0, 2, +)$	$E_t(0, 0, 2, -)$	$p(0, 0, 2, -)$
1.0	1.051 784 087 48(77)	0.486 882	1.552 886 885 83	0.334 332 5	1.560 917 409 665	0.331316537	1.750 004 925 6	0.249997537
	1.051 784 087 4746		1.552 886 885 8238		1.560 917 409 6654		1.750 004 925 5960	
2.0	0.142 456 360 21(08)	0.926 037	0.546 600 746 72	0.673 349	0.574 534 636 379	0.652277061	0.750 074 914 1	0.499925080
	0.142 456 360 20826		0.546 600 746 7126		0.574 534 636 3784		0.750 074 914 1264	
4.0	-0.201 649 288 23	1.675 29	0.038 093 115 38	1.359 274 6	0.111 109 971 587	1.247220956	0.250 988 746 1	0.998020549
	-0.201 649 288 2302		0.038 093 115 3803		0.111 109 971 58626		0.250 988 746 0990	
6.0	-0.260 649 791 31	2.312 11	-0.121 744 444 93	2.0237 84	-0.019 437 228 851	1.781834745	0.087 106 783 3	1.488636608
	-0.260 649 791 3114		-0.121 744 444 95100		-0.019 437 228 851128		0.087 106 783 24228	
8.0	-0.269 021 262 54(37)	2.881 725	-0.188 783 036 57	2.649 628	-0.071 453 569 562	2.267875022	0.008 575 937 0	1.965396909
	-0.269 021 262 5382		-0.188 783 036 58772		-0.071 453 569 562040		0.008 575 936 87662	
10.0	-0.265 432 580 28	3.411 13	-0.219 833 749 01	3.239 73	-0.095 093 601 175	2.716125923	-0.035 171 033 8	2.424721809
	-0.265 432 580 2914		-0.219 833 749 0582		-0.095 093 601 17488		-0.035 171 034 00198	
14.0	-0.255 396 545 98	4.417 514	-0.242 319 086 11	4.344 4	-0.111 495 667 118	3.530338183	-0.078 059 693 0	3.290125373
	-0.255 396 546 2922		-0.242 319 086 1426		-0.111 495 667 11852		-0.078 059 693 28034	
20.0	-0.250 167 097 81	5.917 5	-0.248 752 926 71	5.905 531	-0.113 758 110 521	4.623398216	-0.100 623 878 9	4.479105705
	-0.250 167 098 9774		-0.248 752 926 741		-0.113 758 110 6214		-0.100 623 879 14096	
30.0	-0.249 755 905 14	8.437 72	-0.249 734 619 46	8.437 4	-0.110 960 223 739	6.321870831	-0.109 116 195 2	6.288970023
	-0.249 755 905 4846		-0.249 734 619 4714		-0.110 960 225 79684		-0.109 116 195 34154	
40.0	-0.249 872 858 88	10.952 1	-0.249 872 610 06	10.952 1	-0.110 588 155 306	8.014690427	-0.110 429 620 8	8.010733322
	-0.249 872 859 9708		-0.249 872 610 0936		-0.110 588 156 5852		-0.110 429 620 89928	
50.0	-0.249 928 750 05	13.461 3	-0.249 928 747 50	13.461 26	-0.110 756 575 302	9.706846056	-0.110 745 830 0	9.706500079
	-0.249 928 750 0956		-0.249 928 747 5080		-0.110 756 576 55914		-0.110 745 830 06112	

C. Ellipsoidal nodal surfaces: the $(1, 0, 0, \pm)$ states

The proposed approximation (15) [4] allows us to study the n th excited state in ξ direction with n nodes in the ξ variable. Let us consider the simplest case, $n = 1$ and $\Lambda = 0$ of the parity (\pm) , $(1, 0, 0, \pm)$ or, differently, $2s\sigma_g$ and $3p\sigma_u$, respectively. The main difference with the approximation for the ground state (16) comes due to the presence of a monomial factor $(\xi - \xi_0)$ in the expression for $X_0(\xi)$, while the $Y_0(\eta)$ remains functionally the same,

$$X_0 = \frac{(\xi - \xi_0)}{(\gamma + \xi)^{2 - \frac{R}{p}}} e^{-\xi \frac{\alpha + p\xi}{\gamma + \xi}}. \quad (19)$$

Here ξ_0 defines the position of the node and it can be fixed by imposing the orthogonality condition between these states the $(\pm$ parity) and the lowest states, *i.e.* $\langle (0, 0, 0, \pm) | (1, 0, 0, \pm) \rangle = 0$. The orthogonality with the states $(0, 0, \Lambda, \pm)$ for any Λ is always fulfilled. Eventually, the approximation $\Psi_{1,0,0}^{(\pm)}$ contains six free parameters which are obtained using the variational method. Results are presented in Table VI for the two states $2s\sigma_g$ $(1, 0, 0, +)$ and $3p\sigma_u$ $(1, 0, 0, -)$ as a function of the internuclear distance R . Comparison the variational energy with previous, highly accurate results [18] (given on the second line) for each R -value is presented. The agreement is on the level of 10 s.d. For each state the variational value of p (when p is taken as a variational parameter in (15)) as well as the node position ξ_0^\pm are given. In both cases $(1, 0, 0, \pm)$ the node position is a decreasing function of the internuclear distance having a finite value for small R and conversely approaching to the lower limit in ξ -coordinate, $\xi = 1$ at large R , roughly as $\sim 1/R$. At the point ξ_0^\pm , the wave function (19) vanishes. In the configuration space it corresponds to a nodal surface which is a prolate spheroid of eccentricity $\varepsilon = 1/\xi_0^\pm$.

Functions $X_0(\xi)$, $Y_0^{(\pm)}(\eta)$ and the first corrections to the phases are shown in Figs. 13, 14, 15 and 16 for $R = 2$ a.u. as an illustration.

D. Separation constant A

In developed perturbation theory so as to estimate the accuracy of the approximation (15) for $X_0(\xi)$ and $Y_0(\eta)$, two expressions, one for each variable, for the separation constant are obtained $A_{n,\xi}$ and $A_{n,\eta}$ (see Appendix and Eqs. (35) and (41)). However, the condition of consistency $A_{n,\xi} = A_{n,\eta}$ should be imposed. Table VII presents the separation constant for

TABLE VI: Total energy $E_t(R)$ for the $2s\sigma_g$ (1, 0, 0, +) and $3p\sigma_u$ (1, 0, 0, -) states of the H_2^+ molecular ion (the first line) compared to [18] (the second line).

R(a.u.)	$E_t(1, 0, 0, +)$	$p(1, 0, 0, +)$	ξ_0^+	$E_t(1, 0, 0, -)$	$p(1, 0, 0, -)$	ξ_0^-
1.0	1.154 150 822 6 1.154 150 823 003	0.459850295	2.782853311	1.521 369 039 285 1.521 369 039 2720	0.345916	5.360475264
2.0	0.278 270 249 325 0.278 270 249 323 4	0.849546791	1.907869613	0.489 173 669 829 0.489 173 669 8286	0.714721	2.532742379
4.0	-0.077 029 734 913 5 -0.077 029 734 914 98	1.519249466	1.477672193	0.009 780 899 90 0.009 780 899 904368	1.40031296	1.589362953
6.0	-0.161 775 845 624 -0.161 775 845 629 74	2.110919849	1.330973187	-0.121 531 762 3 -0.121 531 762 33782	2.02331	1.364704127
8.0	-0.193 554 665 734 -0.193 554 665 735 18	2.663995993	1.254298836	-0.174 967 289 16 -0.174 967 289 19184	2.60758	1.265974957
10.0	-0.209 421 251 79 -0.209 421 251 818 4	3.199301689	1.206019531	-0.201 171 505 95 -0.201 171 506 037	3.16691	1.210160770
20.0	-0.236 998 606 92 -0.236 998 606 945 2	5.805158111	1.103266490	-0.236 904 750 195 -0.236 904 750 2114	5.80435	1.103289607
30.0	-0.243 892 622 63 -0.243 892 622 973 6	8.359177003	1.068352565	-0.243 891 770 96 -0.243 891 770 9742	8.35916	1.068352748
40.0	-0.246 478 659 89 -0.246 478 659 911 8	10.889970797	1.051017992	-0.246 478 652 70 -0.246 478 652 7404	10.88997	1.051017930
50.0	-0.247 714 222 867 -0.247 714 222 873 8	13.409749785	1.040679396	-0.247 714 222 80 -0.247 714 222 8160	13.40975	1.040679432

all considered states. For each R -value the first/second line correspond to A_ξ / A_η calculated with (35) / (41) compared to Marcela et al [18] (third row). It turns out that as a result of variational calculations the condition $A_{n,\xi} = A_{n,\eta}$ is fulfilled automatically, up to ~ 8 significant digits which is in agreement with those presented by Marcela et al [18]. Hence, there is no need to impose the equality condition. It is a reflection of the outstanding

accuracy of the approximation (15).

III. TRANSITIONS

Knowledge of wave functions with high local relative accuracy $\lesssim 10^{-5} - 10^{-6}$ gives us a chance to calculate matrix elements with controlled relative accuracy $\lesssim 10^{-5} - 10^{-6}$. As a demonstration we calculate E1, E2 and B1 Oscillator Strength as a function of interproton distance for the permitted radiative transitions from excited states to the ground state $1s\sigma_g(0,0,0,+)$.

A. E1 Oscillator Strength

Following Bates [20, 21], with the energy given in Rydbergs, the electric dipole oscillator strength from a lower electronic (initial) state Ψ_i to an upper electronic (final) state Ψ_f , is given by

$$f_{i \rightarrow f}^{(E1)}(R) = \frac{1}{3} G (E_f(R) - E_i(R)) \mathbf{S}_{if}^{(1)}, \quad (20)$$

where G is the orbital degeneracy factor, $\mathbf{S}_{if}^{(1)}(R)$ is the square of the matrix element

$$\mathbf{S}_{if}^{(1)}(R) = |\langle \Psi_i(R) | \mathbf{r} | \Psi_f(R) \rangle|^2,$$

and \mathbf{r} is the vector of the electron position measured from the interproton midpoint. The involved excited states for permitted electric dipole transitions from the ground state $1s\sigma_g$ are the states $2p\sigma_u$, $2p\pi_u$ and $3p\sigma_u$. In Table VIII the E1 oscillator strength is presented for two transitions: $1s\sigma_g - 2p\pi_u$ and $1s\sigma_g - 3p\sigma_u$. The transition $1s\sigma_g - 2p\sigma_u$ was calculated and discussed in [4] and we won't present here the results. The orbital degeneracy factor is $G = 2$ for $f_{1s\sigma_g-2p\pi_u}$ and $G = 1$ for $f_{1s\sigma_g-3p\sigma_u}$. It is assumed this calculation should provide at least 5 s.d. correctly. As a result for all internuclear distances they coincide in 6 s.d. with Tsogbayar et al, [16] for $1s\sigma_g - 2p\pi_u$ (with an exception at $R=1$ a.u. where it deviates in one unit at the 6th digit) which increases up to 7 figures for intermediate R . The E1 oscillator strength $f_{1s\sigma_g-3p\sigma_u}$ is compared with Bates et al [21] only for two values of $R = 2, 4$ a.u. and the agreement is in 2 s.d. We also confirm the striking qualitative result by Bates et al that the E1 oscillator strength increases in ~ 20 times coming from $R = 2$ a.u. to 4 a.u.

TABLE VII: Separation parameters $A_{1,\xi}$ (first row), $A_{1,\eta}$ (second row) for all the sates considered of the H_2^+ -ion compared to Marcela et al [18](third row).

	(000+)	(000-)	(001+)	(001-)	(002+)	(002-)	(100+)	(100-)
R	$1s\sigma_g$	$2p\sigma_u$	$2p\pi_u$	$3d\pi_g$	$3d\delta_g$	$4f\delta_u$	$2s\sigma_g$	$3p\sigma_u$
1.0	0.2499462430	-1.8300104198	0.0476692616	-3.9520464219	0.0157049965	-5.9791583275	0.0711543055	-1.9281072878
	0.2499462409	-1.8300104197	0.0476693150	-3.9520464344	0.0157049889	-5.9791583064	0.0711543140	-1.9281072817
	0.2499462406113	-1.830010419730	0.047669315711	-3.952046434393	0.015704988875	-5.979158306119	0.071154314127	-1.928107280448
2.0	0.8117295877	-1.1868893947	0.1749484742	-3.8048856116	0.0611354153	-5.9165512457	0.2484661667	-1.6917231809
	0.8117295852	-1.1868893929	0.1749484725	-3.8048856050	0.0611354010	-5.9165512311	0.2484661712	-1.6917231733
	0.8117295846248	-1.186889392359	0.174948472433	-3.804885604702	0.061135400906	-5.916551230876	0.248466171440	-1.691723172798
4.0	2.7995887561	1.5384644804	0.6001486772	-3.1948053489	0.2270652065	-5.6657454590	0.8535318015	-0.7976034401
	2.7995887582	1.5384644803	0.6001486748	-3.1948053506	0.2270652107	-5.6657454689	0.8535318003	-0.7976034382
	2.799588759471	1.538464480300	0.600148674671	-3.194805350518	0.227065210827	-5.665745469006	0.853531800197	-0.797603437898
6.0	6.4536037434	5.9279301781	1.2199716980	-2.1786687874	0.4743694112	-5.2501595578	1.8115068883	0.5663869192
	6.4536037423	5.9279301759	1.2199717011	-2.1786687836	0.4743694166	-5.2501595612	1.8115068932	0.5663869192
	6.453603742887	5.927930173726	1.219971701568	-2.178668782566	0.474369416805	-5.250159561131	1.811506894227	0.566386919545
8.0	12.2261746132	12.0646853402	2.0537173294	-0.7961022597	0.7914989890	-4.6781903409	3.2069680505	2.3733521986
	12.2261746118	12.0646853394	2.0537173246	-0.7961022613	0.7914989805	-4.6781903532	3.2069680527	2.3733521972
	12.22617461542	12.06468533824	2.053717323829	-0.7961022613695	0.791498980083	-4.678190353126	3.206968053370	2.373352197778
10.0	20.1333096527	20.0921239053	3.1610270665	0.9355443423	1.1760019683	-3.9601419353	5.1293596287	4.6288376336
	20.1333042259	20.0921157054	3.1610270649	0.9355443394	1.1760019677	-3.9601419604	5.1293596245	4.6288376291
	20.13329317839	20.09209890008	3.161027064845	0.9355443386850	1.176001967652	-3.960141960690	5.129359623687	4.628837627894
20.0	90.0528911866	90.0528775638	15.6431425753	15.4372141472	4.4202357771	1.6768434995	23.1467951638	23.1310108444
	90.0528911837	90.0528775637	15.6431424784	15.4372141468	4.4202357567	1.6768434549	23.1467951625	23.1310108423
	90.05289119141	90.05287756706	15.64314256883	15.43721414965	4.420235762270	1.676843453846	23.14679516399	23.13101084191
30.0	210.0345966014	210.0345966014	41.5927047072	41.5865009061	11.8536327107	11.1439910435	54.1918175098	54.1915412139
	210.0345965987	210.0345965997	41.5927046648	41.5865009042	11.8536321491	11.1439910147	54.1918174666	54.1915412094
	210.0345965903	210.0345965883	41.59270470411	41.58650090379	11.85363268535	11.14399101596	54.19181751174	54.19154120499
40.0	380.0257071902	380.0257071902	80.2475884726	80.2474668189	25.5692520539	25.4727279329	97.8369229167	97.8369191379
	380.0257071899	380.0257071899	80.2475883011	80.2474668173	25.5692515860	25.4727279007	97.8369229125	97.8369191305
	380.0257071871	380.0257071871	80.24758848264	80.24746682685	25.56925202708	25.47272792120	97.83692292343	97.83691912308
50.0	600.0204520196	600.0204516482	131.4445904451	131.4445885530	45.2845813578	25.4727279329	154.0220957323	154.0220957009
	600.0204519899	600.0204516470	131.4445904398	131.4445885530	45.2845807868	25.4727279007	154.0220957308	154.0220956952
	600.0204516331	600.0204516331	131.4445904563	131.4445885619	45.28458134150	45.27511009129	154.0220957319	154.0220956865

TABLE VIII: Electric dipole oscillator strength for transition $1s\sigma_g - 2p\pi_u$ and $1s\sigma_g - 3p\sigma_u$ vs R compared to Tsogbayar et al [16] and Bates et al [21] (rounded).

R	$f_{1s\sigma_g-2p\pi_u} \times 10^{-1}$			$f_{1s\sigma_g-3p\sigma_u} \times 10^{-2}$		
	Present	[16]		Present	[21]	
1.0	3.934 370 22	3.934 381 322		2.203 421 96		
2.0	4.601 871 35	4.601 869 855		$8.249\ 067\ 00 \times 10^{-2}$	8.24×10^{-2}	
4.0	4.655 236 69	4.655 237 278		1.614 379 52	1.61	
6.0	3.841 069 41	3.841 069 351		4.145 987 07		
8.0	3.035 614 09	3.035 614 626		5.567 828 37		
10.0	2.617 504 44	2.617 505 281		6.106 005 25		
20.0	2.717 465 95	2.717 469 205		6.503 362 27		
30.0	2.774 375 78			6.610 830 83		
40.0	2.775 806 83			6.673 398 05		
50.0	2.775 499 12			6.715 284 57		

B. B1 Oscillator Strength

It is known that the magnetic dipole transitions are much smaller than the electric dipole transition. The magnetic dipole B1 Oscillator Strength, with the energy in Rydbergs, is given by

$$f_{i \rightarrow f}^{(B1)}(R) = \frac{1}{3} (E_f(R) - E_i(R)) |\mathbf{S}(R)|^2, \quad (21)$$

where $\mathbf{S}(R)$ is the matrix element

$$\mathbf{S}(R) = -\mu_B \langle \Psi_i(R) | \mathbf{L} | \Psi_f(R) \rangle,$$

\mathbf{L} is the angular momentum operator and μ_B is the Bohr magneton. Between the states we consider at present article, there is only one permitted magnetic dipole transition from the ground state to $f_{1s\sigma_g-3d\pi_g}$. This B1 Oscillator strength is presented in Table IX. Comparison is made with previously known results by Dalgarno et al. [19] at $R = 2, 4a.u.$ only with 3 s.d. We confirm the striking qualitative observation that the B1 oscillator strength increases in ~ 10 times coming from $R = 2a.u.$ to $4a.u.$

TABLE IX: Magnetic dipole oscillator strength for transition $1s\sigma_g - 3d\pi_g$ vs R compared to Dalgarno et al. [19].

$f_{1s\sigma_g-3d\pi_g}$	
R	Present [19]
1.0	1.050 606 8 E-08
2.0	1.666 176 0 E-07 1.67 E-07
4.0	2.008 469 0 E-06 2.01 E-06
6.0	6.251 641 6 E-06
8.0	1.129 235 3 E-05
10.0	1.633 841 0 E-05
20.0	5.260 000 6 E-05
30.0	1.169 171 1 E-04
40.0	2.078 469 5 E-04
50.0	3.247 423 8 E-04

C. E2 Oscillator Strength

It is known that the electric quadrupole transitions are much smaller than the electric dipole transition but comparable with magnetic dipole transitions. For the first time we calculate electric quadrupole transitions in H_2^+ molecular ion for transitions $1s\sigma_g - 3d\pi_g$, $1s\sigma_g - 3d\delta_g$ and $1s\sigma_g - 2s\sigma_g$.

The electric quadrupole E2 oscillator strength with the energy in Rydbergs is given by

$$f_{i \rightarrow f}^{(E2)}(R) = \frac{\alpha^2}{240} G (E_f(R) - E_i(R))^3 \mathbf{S}_{if}^{(2)}(R), \quad (22)$$

where $\mathbf{S}_{if}^{(2)}(R)$ is the square of the matrix element of the electric quadrupole moment and α is the fine structure constant. The orbital degeneracy factor is $G = 2$ for $f_{1s\sigma_g-3d\pi_g}$ and $f_{1s\sigma_g-3d\delta_g}$ and $G = 1$ for $f_{1s\sigma_g-2s\sigma_g}$. It is assumed this calculation should provide at least 5 s.d. correctly. Results are presented in Table X. Comparing the electric dipole transition $f_{1s\sigma_g-2p\pi_u}$, see Table VIII with the magnetic dipole transition $f_{1s\sigma_g-3d\pi_g}$, see Table IX, and electric quadrupole transition $f_{1s\sigma_g-3d\pi_g}$, see Table X oscillator strengths, one can see that

at $R = 2a.u.$ the E1 oscillator strength is six orders of magnitude larger than E2 oscillator strength and seven order of magnitude larger than B1.

TABLE X: Quadrupole oscillator strength f for transitions $1s\sigma_g - 3d\pi_g$, $1s\sigma_g - 3d\delta_g$ and $1s\sigma_g - 2s\sigma_g$ vs R .

R	$f_{1s\sigma_g-3d\pi_g}$	$f_{1s\sigma_g-3d\delta_g}$	$f_{1s\sigma_g-2s\sigma_g}$
1.0	1.500 688 2 E-06	1.240 332 8 E-06	1.386 514 0 E-09
2.0	2.608 637 5 E-06	1.557 357 3 E-06	1.378 379 7 E-08
4.0	4.539 815 8 E-06	1.436 910 5 E-06	1.372 684 3 E-07
6.0	6.122 024 1 E-06	9.655 519 1 E-07	5.240 450 5 E-07
8.0	7.884 701 2 E-06	5.901 755 7 E-07	1.222 375 2 E-06
10.0	1.010 476 3 E-05	3.817 367 8 E-07	2.179 700 3 E-06
20.0	3.114 396 7 E-05	1.558 008 9 E-07	9.918 089 5 E-06
30.0	6.984 147 5 E-05	1.735 371 6 E-07	2.253 646 5 E-05
40.0	1.244 746 2 E-04	1.864 752 8 E-07	4.027 405 2 E-05
50.0	1.946 579 9 E-04	1.879 848 1 E-07	6.317 650 4 E-05

D. H_2^+ molecular ion in the united atomic ion He^+ limit

When for H_2^+ molecular ion the internuclear distance tends to zero, $R \rightarrow 0$, we arrive at one-electron atomic system with nuclear charge $Z = 2$, *i.e.* the He^+ ion. In practice, at $R \rightarrow 0$ we have

$$\lim_{R \rightarrow 0} R\xi = 2r, \quad 0 \leq r \leq \infty, \quad (23)$$

$$\lim_{R \rightarrow 0} \eta = \cos \theta, \quad 0 \leq \theta \leq \pi, \quad (24)$$

$$\lim_{R \rightarrow 0} \phi = \phi, \quad 0 \leq \phi \leq 2\pi, \quad (25)$$

where (r, θ, ϕ) are the spherical coordinates. However, although in this limit the parameter $p \rightarrow 0$, the ratio

$$\lim_{R \rightarrow 0} \frac{R}{p} = \frac{2}{\sqrt{-E}} = \frac{2n}{Z} \bigg|_{Z=2} = n, \quad (26)$$

(cf. (8)), takes a finite value; here $E = -\mathcal{Z}^2/\mathbf{n}^2$ is the total energy of the hydrogen-like atom of \mathcal{Z} -charge ($\mathcal{Z} = 2$) with principal quantum number \mathbf{n} . Now taking the variational parameters $\alpha \rightarrow 0$, $\gamma \sim \text{const}$, $a_1 \rightarrow 0$, $b_2 = b_3 \rightarrow 0$, the limit of approximation (15) at $R \rightarrow 0$ (up to a normalization factor) is

$$\Psi_{n,m,\Lambda;\mathbf{n}}^{(\pm)} \propto r^{\mathbf{n}-n-1} P_n(r) e^{-\frac{2}{\mathbf{n}}r} \sin^\Lambda \theta Q_m(\cos^2 \theta) \begin{bmatrix} 1 \\ \cos \theta \end{bmatrix} e^{\pm i\Lambda\phi}. \quad (27)$$

This formulas realizes the correspondence between the states of the molecular ion H_2^+ and ones of the atomic ion He^+ . The examples of this correspondence are displayed in Table XI. The first column presents the molecular orbital (n, m, Λ, \pm) approximated by (15). Its united atom nomenclature is given in the second column. In the limit $R \rightarrow 0$ this approximation takes the form (27) (third column). Clearly, these functions coincide to the exact wavefunctions of the atomic ion He^+ (up to normalization factor), when the constant c in the polynomial $P_n(r)$ (when present) takes a certain value (see the fourth column). Hence, the molecular orbital (n, m, Λ, \pm) in approximation ((15)) in the limit $R \rightarrow 0$ corresponds to the exact atomic orbital $(\mathbf{n}, \mathbf{l}, \mathbf{m})$ with appropriate value of l , see the last column Table XI.

IV. CONCLUSIONS

Summarizing we want to state that a simple uniform approximation of the eigenfunctions for the H_2^+ molecular ion is presented. It allows us to calculate any expectation value or matrix element with guaranteed accuracy. It manifests the approximate solution of the problem of spectra of the H_2^+ molecular ion. In a quite straightforward way similar approximations can be constructed for general two-center, one-electron system (Z_a, Z_b, e) , in particular, for $(\text{HeH})^{++}$. It will be done elsewhere.

The key element of the procedure is to construct an interpolation between the WKB expansion at large distances and perturbation series at small distances for the phase of the wavefunction. Or, in other words, to find an approximate solution for the corresponding eikonal equation. Separation of variables allowed us to solve this problem. In the case of non-separability of variables the WKB expansion of a solution of the eikonal equation can not be constructed in unified way, since all depends on the way to approach to infinity. However, a reasonable approximation of the first growing terms of the WKB expansion seems sufficient to construct the interpolation between large and small distances giving high

TABLE XI: Correspondence between the molecular orbital (n, m, Λ, \pm) and the atomic orbital $(\mathbf{n}, 1, \mathbf{m})$ in the limit $R \rightarrow 0$. The molecular approximation (15) takes the form (27), where c is the constant term in the polynomial.

Molecular Orbital United Atom			Atomic Orbital	
(n, m, Λ, \pm)	Designation (27)	c	$(\mathbf{n}, 1, \mathbf{m})$	
$(0, 0, 0, +)$	$1s\sigma_g$	e^{-2r}	$(1, 0, 0)$	
$(0, 0, 0, -)$	$2p\sigma_u$	$re^{-r} \cos \theta$	$(2, 1, 0)$	
$(0, 0, 1, +)$	$2p\pi_u$	$re^{-r} \sin \theta e^{i\phi}$	$(2, 1, 1)$	
$(0, 0, 1, -)$	$3d\pi_g$	$r^2 e^{-\frac{2}{3}r} \sin \theta \cos \theta e^{i\phi}$	$(3, 2, 1)$	
$(0, 0, 2, +)$	$3d\delta_g$	$r^2 e^{-\frac{2}{3}r} \sin^2 \theta e^{2i\phi}$	$(3, 2, 2)$	
$(0, 0, 2, -)$	$4f\delta_u$	$r^3 e^{-\frac{1}{2}r} \sin^2 \theta \cos \theta e^{2i\phi}$	$(4, 3, 2)$	
$(1, 0, 0, +)$	$2s\sigma_g$	$(r - c)e^{-2r}$	2	$(2, 0, 0)$
$(1, 0, 0, -)$	$3p\sigma_u$	$r(r - c)e^{-\frac{2}{3}r} \cos \theta$	3	$(3, 1, 0)$
$(0, 1, 0, +)$	$3d\sigma_g$	$r^2 e^{-\frac{2}{3}r} (\cos^2 \theta - c)$	1/3	$(3, 2, 0)$
$(0, 1, 0, -)$	$4f\sigma_u$	$r^3 e^{-\frac{1}{2}r} (\cos^2 \theta - c) \cos \theta$	3/5	$(4, 3, 0)$

accuracy results. This program was realized for the problem of the hydrogen atom in a magnetic field and will be published elsewhere.

It is worth mentioning a curious fact that the problem (3) possesses the hidden algebra $sl(2) \oplus sl(2)$. It can be immediately seen - making the gauge rotation of the operators in r.h.s. of the equations (6) and (7) with gauge factors $e^{-p\xi}$ and $e^{p\eta}$, respectively. We obtain the operators which are in the universal enveloping algebra of $sl(2)$ (see e.g. [17]). The dimension of the representation is $-\Lambda$ and $-\Lambda + \frac{R}{p}$, respectively. For non-physical values of Λ and integer ratio $\frac{R}{p}$ the algebras $sl(2)$ appear in the finite-dimensional representation realized in action on polynomials in ξ, η . It explains a mystery sometimes observed of the existence of polynomial solutions for non-physical values of Λ in the problem (2) (details will be given elsewhere).

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Appendix

The easiest way to calculate a deviation of the approximation from the exact eigenfunction is to develop a perturbation theory in framework of the so-called *non-linearization procedure* [14]: for a chosen approximation ψ_0 a corresponding potential $V_0 = \frac{\Delta\psi_0}{\psi_0}$ is found with $E_0 = 0$, for which ψ_0 is the exact eigensolution. Then the potential is written in the form $V = V_0 + \lambda V_1$, then it is looked for energy and the eigenfunction in the form of power series in the parameter λ , $E = \sum \lambda^n E_n$ and $\Psi = \Psi_0 \exp(-\sum \lambda^n \varphi_n)$, respectively. Eventually, λ is placed equal to one.

Due to specifics of (1) because of the separation of variables the procedure can be developed for both functions X and Y (see (5)) separately as well as for the separation parameter A , while keeping the energy E fixed. It can be done for the system of equations (6), (7). As a first step let us transform (6), (7) into the Riccati form by introducing $X = fe^{-\varphi}$ and $Y = ge^{-\varrho}$, respectively,

$$(\xi^2 - 1)[f(x' - x^2) + 2f'x - f''] + 2(\Lambda + 1)\xi[fx - f'] = [A - V(\xi)]f, \quad x = \varphi'_\xi \quad (28)$$

where the "potential" $V(\xi) = p^2\xi^2 - 2R\xi$, and

$$(\eta^2 - 1)[g(y' - y^2) + 2g'y - g''] + 2(\Lambda + 1)\eta[gy - g'] = [A - W(\eta)]g, \quad y = \varrho'_\eta \quad (29)$$

where the "potential" $W(\eta) = p^2\eta^2$.

Let us choose some $x_0(\xi) = \varphi'_0(\xi)$, then substitute it to the l.h.s. of (28) and call the result as unperturbed "potential" $V_0(\xi)$ putting without loss of generality $A_0 = 0$. The difference between the original $V(\xi)$ and generated $V_0(\xi)$ is the perturbation, $V_1(\xi) = V(\xi) - V_0(\xi)$. For a sake of convenience we can insert a parameter λ in front of V_1 and develop the perturbation

theory in powers of it. The perturbation theory is also developed for node states where a node position is also looked for the form of power expansion in λ .

$$x = \sum \lambda^n x_n, \quad f = \sum \lambda^n f_{n,\xi}, \quad A = \sum \lambda^n A_{n,\xi}. \quad (30)$$

The equation for n th correction has a form,

$$\left\{ (\xi^2 - 1)^{\Lambda+1} X_0^2 \left[x_n - \left(\frac{f_{n,\xi}}{f_{0,\xi}} \right)' \right] \right\}' = (\xi^2 - 1)^\Lambda X_0^2 [A_{n,\xi} - Q_n], \quad (31)$$

where $Q_1 = V_1$ and

$$\begin{aligned} Q_n = & -(\xi^2 - 1) \sum_{i=1}^{n-1} x_i x_{n-i} \\ & - \frac{1}{f_{0,\xi}} \left[\sum_{k=1}^{n-1} f_{k,\xi} \left((\xi^2 - 1) \sum_{i=0}^{n-k} x_i x_{n-k-i} - \frac{((\xi^2 - 1)^{\Lambda+1} x_{n-k})'}{(\xi^2 - 1)^\Lambda} + A_{n-k,\xi} - V_{n-k} \right) \right. \\ & \left. - 2(\xi^2 - 1) \sum_{k=1}^{n-1} x_k f'_{n-k,\xi} \right], \end{aligned} \quad (32)$$

for $n > 1$. Integrating (31) we obtain

$$x_n = \left(\frac{f_{n,\xi}}{f_{0,\xi}} \right)' + \frac{1}{(\xi^2 - 1)^{\Lambda+1} X_0} \int_1^\xi (A_{n,\xi} - Q_n) (\xi^2 - 1)^\Lambda X_0^2 d\xi, \quad (33)$$

where $f_{n,\xi}$ and $A_{n,\xi}$ are obtained in the same way. These are

$$f_{n,\xi}(\xi_0) = \frac{1}{(\xi_0^2 - 1)^{\Lambda+1} e^{-2\varphi_0} f'_{0,\xi}(\xi_0)} \int_1^{\xi_0} (A_{n,\xi} - Q_n) (\xi^2 - 1)^\Lambda X_0^2 d\xi, \quad (34)$$

and

$$A_{n,\xi} = \frac{\int_1^\infty Q_n (\xi^2 - 1)^\Lambda X_0^2 d\xi}{\int_1^\infty (\xi^2 - 1)^\Lambda X_0^2 d\xi}. \quad (35)$$

In a similar way by choosing $y_0(\eta) = \varrho'_0(\eta)$, building the unperturbed "potential" $W_0(\eta)$ and putting $A_0 = 0$ as zero approximation one can develop perturbation theory in the equation (29)

$$y = \sum \lambda^n y_n, \quad g = \sum \lambda^n g_{n,\eta}, \quad A = \sum \lambda^n A_{n,\eta}. \quad (36)$$

The equation for n th correction has a form similar to (31),

$$\left\{ (\eta^2 - 1)^{\Lambda+1} Y_0^2 \left[y_n - \left(\frac{g_{n,\eta}}{g_{0,\eta}} \right)' \right] \right\}' = (\eta^2 - 1)^\Lambda Y_0^2 [A_{n,\eta} - Q_n], \quad (37)$$

where $Q_1 = W_1$ and

$$\begin{aligned}
Q_n = & -(\eta^2 - 1) \sum_{i=1}^{n-1} y_i y_{n-i} \\
& - \frac{1}{g_{0,\eta}} \left[\sum_{k=1}^{n-1} g_{k,\eta} \left((\eta^2 - 1) \sum_{i=0}^{n-k} y_i y_{n-k-i} - \frac{((\eta^2 - 1)^{\Lambda+1} y_{n-k})'}{(\eta^2 - 1)^\Lambda} + A_{n-k,\eta} - V_{n-k} \right) \right. \\
& \left. - 2(\eta^2 - 1) \sum_{k=1}^{n-1} y_k g'_{n-k,\eta} \right], \tag{38}
\end{aligned}$$

for $n > 1$. Its solution is given by (cf.(33))

$$y_n = \left(\frac{g_{n,\eta}}{g_{0,\eta}} \right)' + \frac{1}{(\eta^2 - 1)^{\Lambda+1} Y_0} \int_{-1}^{\eta} (A_{n,\eta} - Q_n)(\eta^2 - 1)^\Lambda Y_0^2 d\eta, \tag{39}$$

where $g_{n,\eta}$ and $A_{n,\eta}$ are obtained in the same way. These are (cf.(34) and (35))

$$g_{n,\eta}(\eta_0) = \frac{1}{(\eta_0^2 - 1)^{\Lambda+1} e^{-2\varrho_0} g'_{0,\eta}(\eta_0)} \int_1^{\eta_0} (A_{n,\eta} - Q_n)(\eta^2 - 1)^\Lambda Y_0^2 d\eta, \tag{40}$$

and

$$A_{n,\eta} = \frac{\int_{-1}^1 Q_n(\eta^2 - 1)^\Lambda Y_0^2 d\eta}{\int_{-1}^1 (\eta^2 - 1)^\Lambda Y_0^2 d\eta}. \tag{41}$$

In order to realize this perturbation theory a condition of consistency should be imposed

$$A_{n,\xi} = A_{n,\eta}. \tag{42}$$

This condition allows us to find the parameter p and, hence, the energy E' and E (see (8)).

Sufficient condition for such a perturbation theory to be convergent is to require a perturbation "potential" to be bounded,

$$|V_1(\xi)| \leq C_\xi, \quad |W_1(\eta)| \leq C_\eta, \tag{43}$$

where C_ξ, C_η are constants. Obviously, that the rate of convergence gets faster with smaller values of C_ξ, C_η . It is evident that the perturbations $V_1(\xi)$ and $W_1(\eta)$ get bounded if $\varphi_0(\xi)$ and $\varrho_0(\eta)$ are smooth functions vanishing at the origin but reproduce exactly the growing terms at $|\xi|, |\eta|$ tending to infinity in (11), (13), respectively.

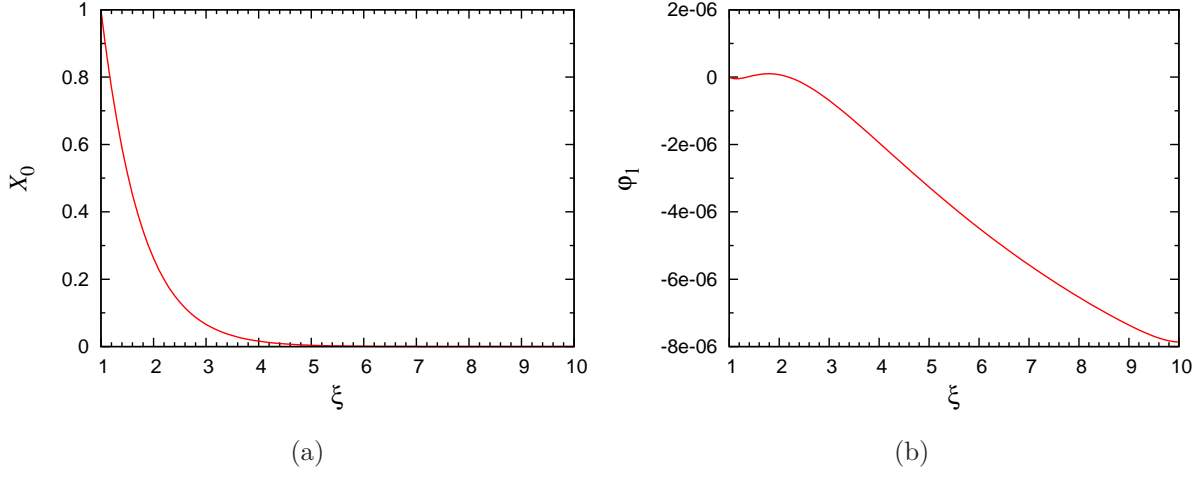


FIG. 1: The $1s\sigma_g$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

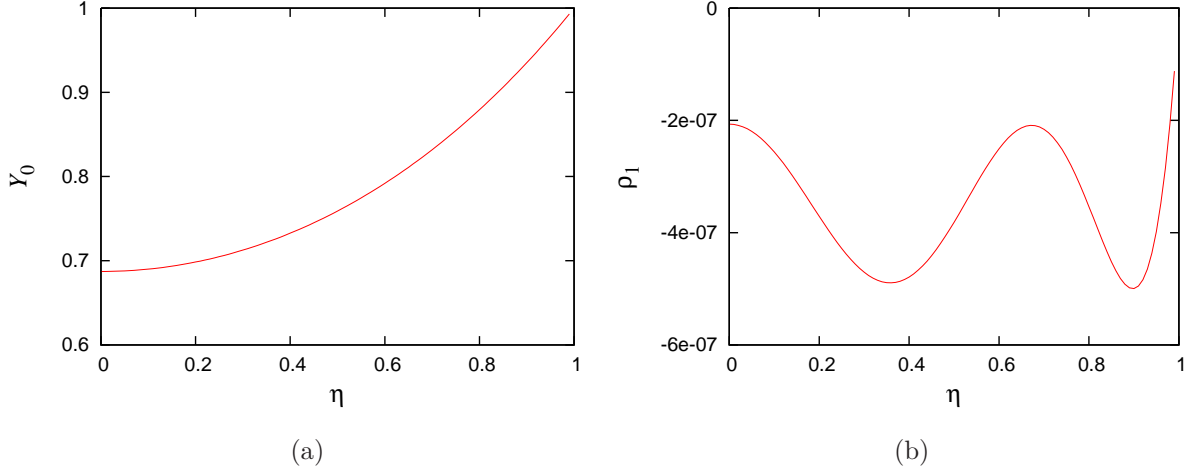


FIG. 2: The $1s\sigma_g$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(+)}$ (16) and (b) the first correction ρ_1 (see (17)).

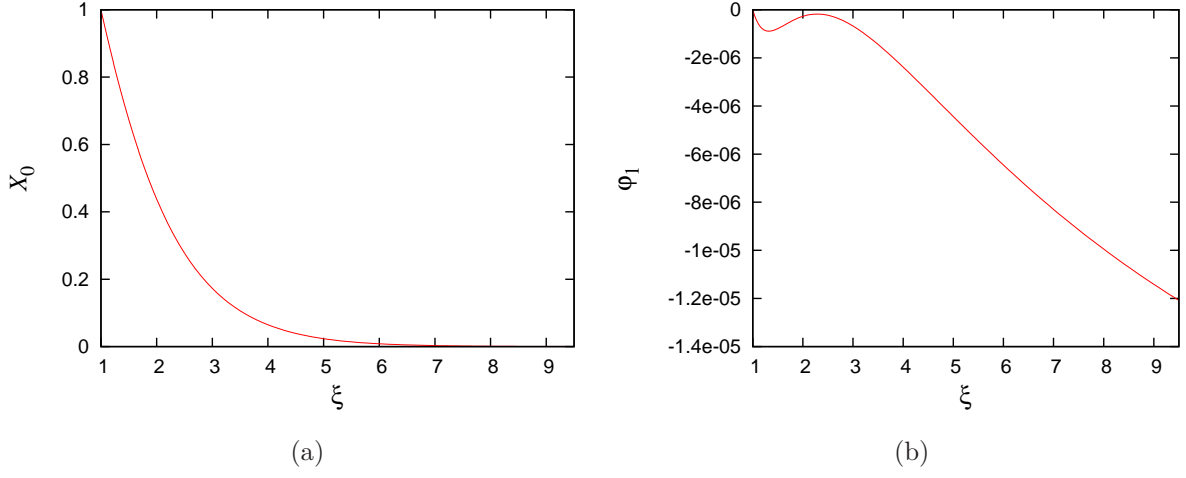


FIG. 3: The $2p\sigma_u$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

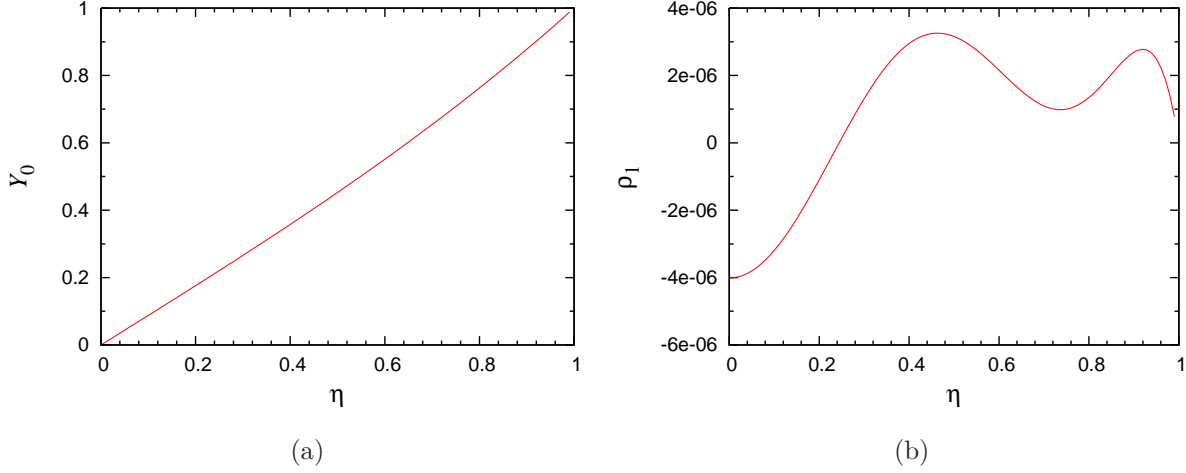


FIG. 4: The $2p\sigma_u$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

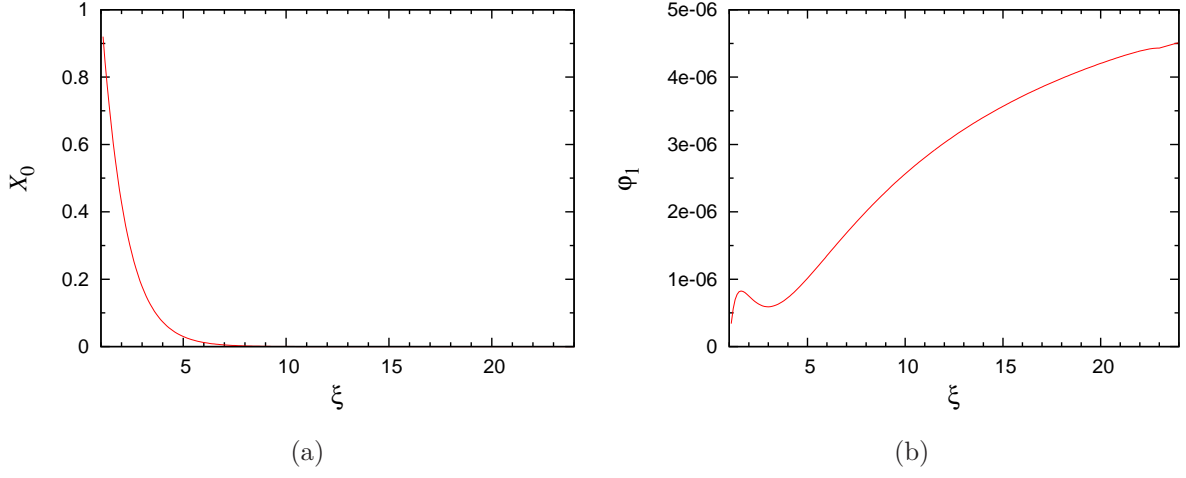


FIG. 5: The $2p\pi_u$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

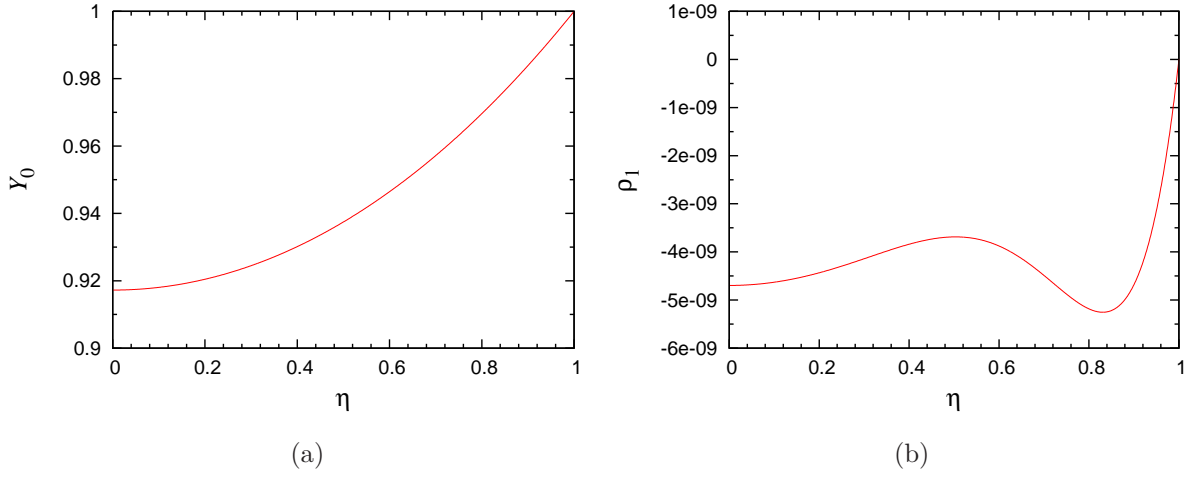


FIG. 6: The $2p\pi_u$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

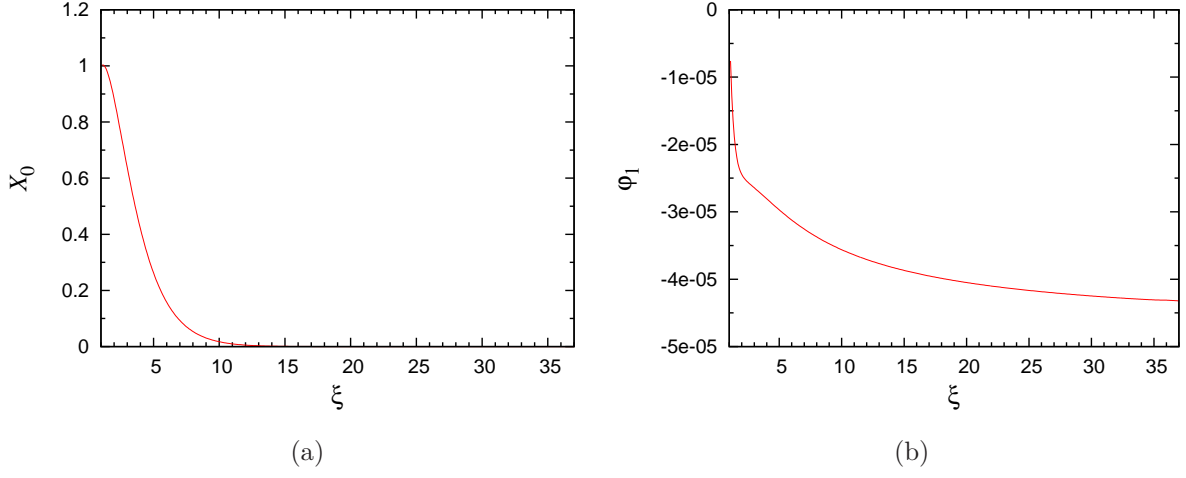


FIG. 7: The $3d\pi_g$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

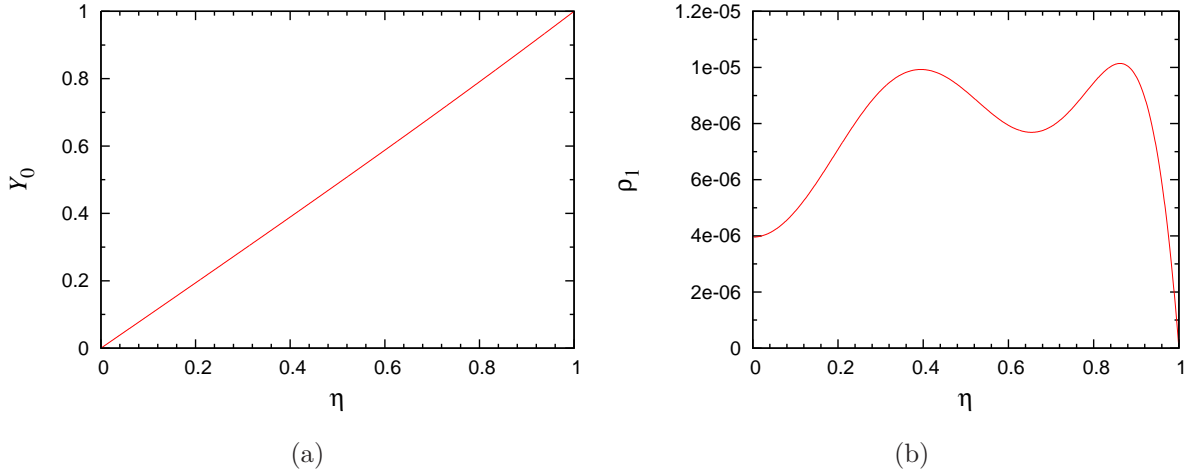


FIG. 8: The $3d\pi_g$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

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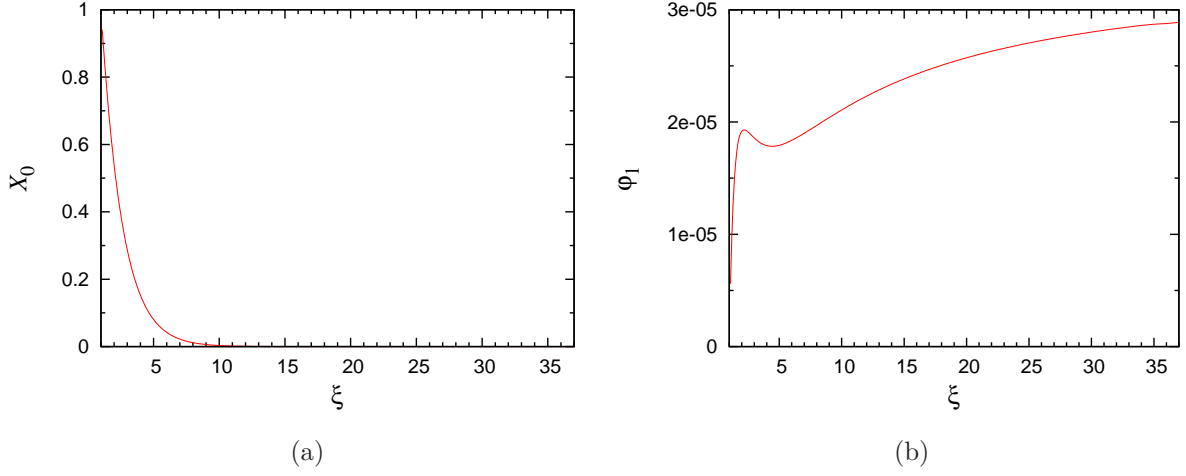


FIG. 9: The $3d\delta_g$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

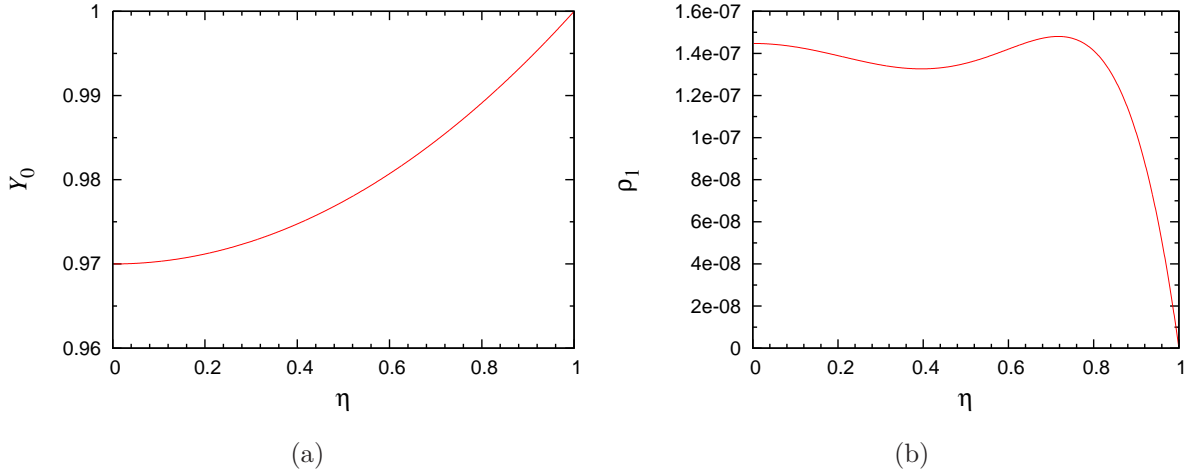


FIG. 10: The $3d\delta_g$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

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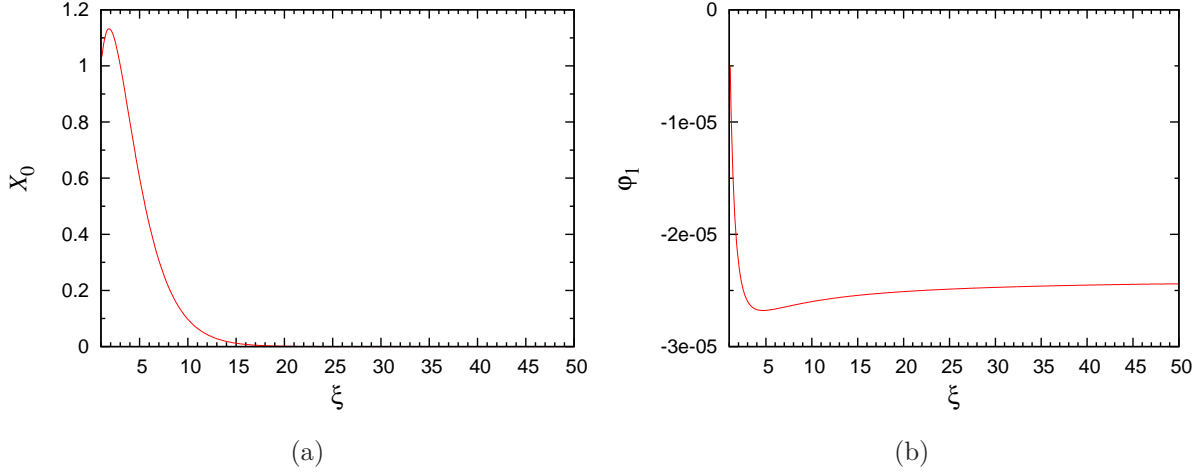


FIG. 11: The $4f\delta_u$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

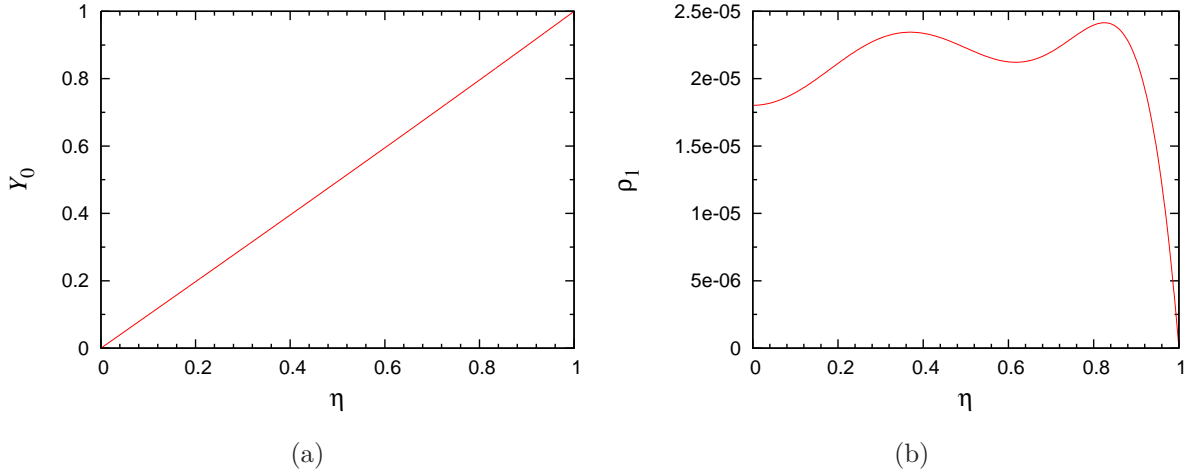


FIG. 12: The $4f\delta_u$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

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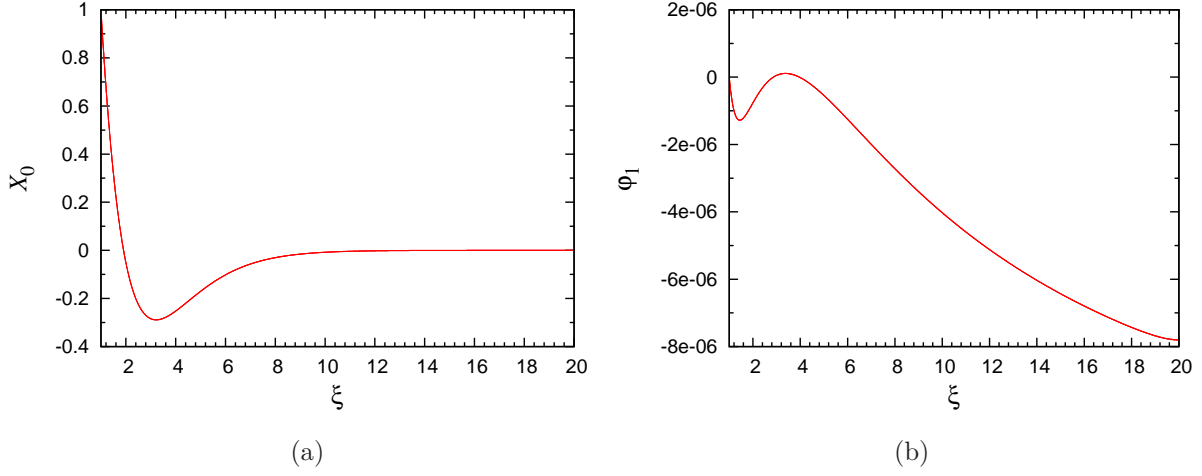


FIG. 13: The $2s\sigma_g$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

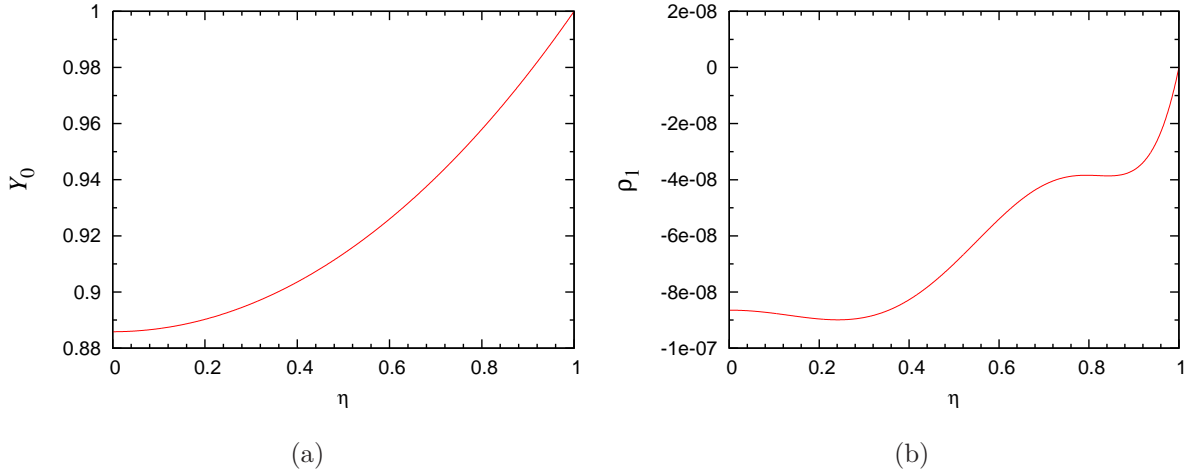


FIG. 14: The $2s\sigma_g$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

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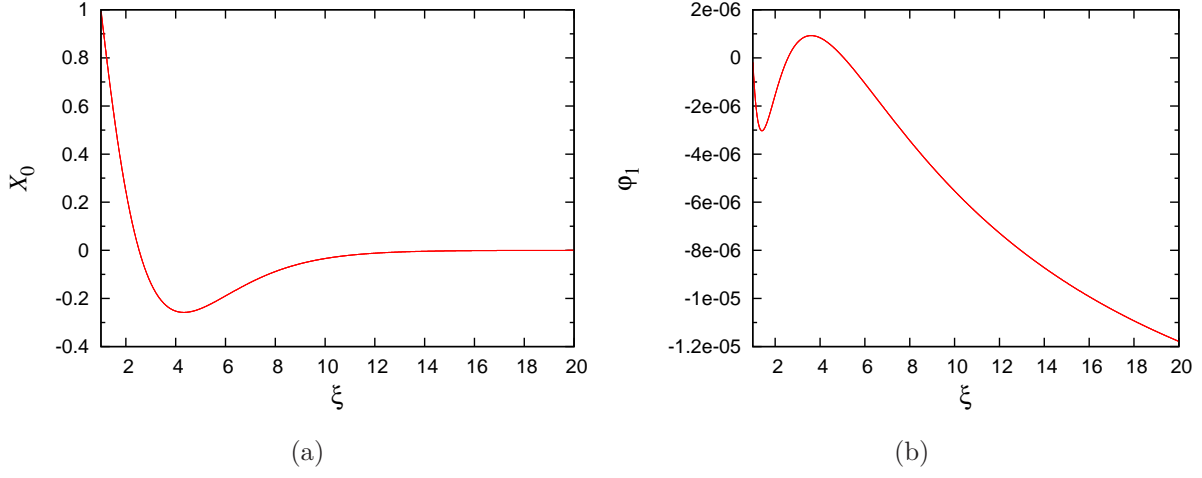


FIG. 15: The $3p\sigma_u$ state at $R = 2$ a.u.: (a) ξ -dependent function X_0 (16) and (b) the first correction φ_1 (see (17)).

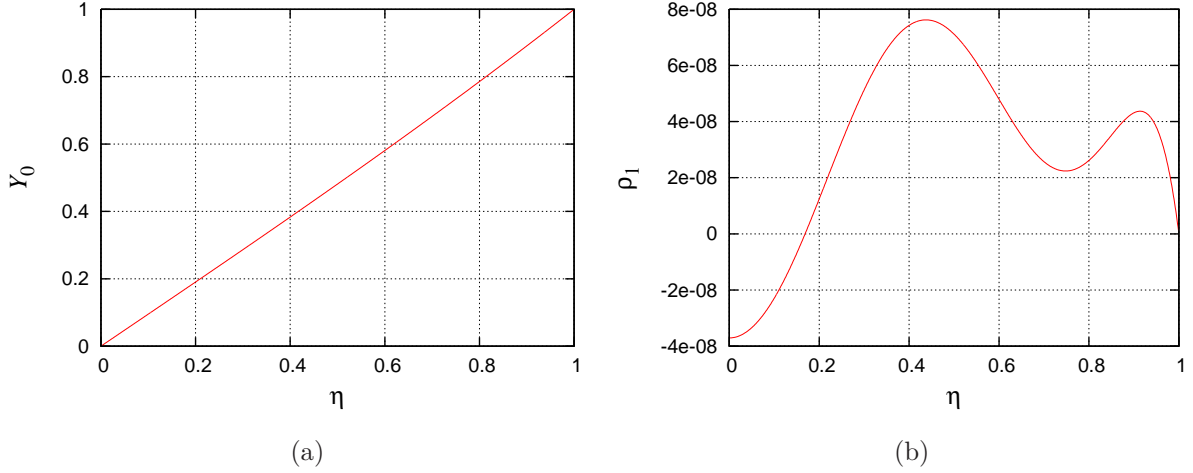


FIG. 16: The $3p\sigma_u$ state at $R = 2$ a.u.: (a) η -dependent function $Y_0^{(-)}$ (16) and (b) the first correction ρ_1 (see (17)).

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